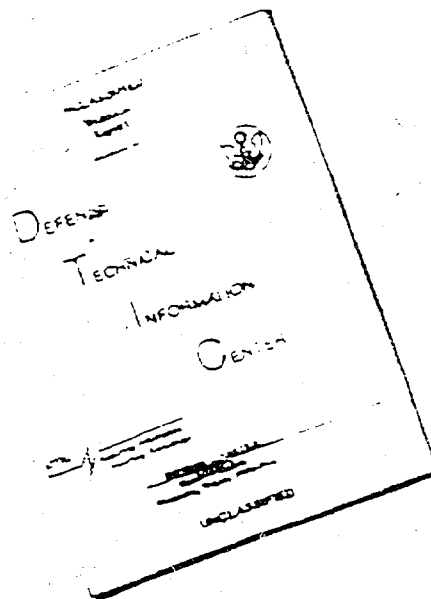ANJJ# 3390:3

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TUBE STUDY OF THE HYDROGEN–OXYGEN REACTION*

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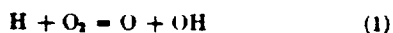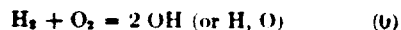*Department of Chemistry, The University of Texas, Austin, Texas*

AND

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: hydrogen–oxygen reaction was investigated using OH absorption and emission meas-
nts of induction times over the temperature range of 1400°–2500°K. The depen ' nce
uction time on composition was studied to measure the relative influence of hydrogen
xygen concentrations in determining the induction times. Comparison of experimental
irements with computed values obtained from an analytic solution to the rate equa-
which is presented in detail, showed that the results could be understood in terms of
oefficient parameters which are in agreement with previous studies. The effect of slow
ional relaxation of O₂ was investigated under conditions where the vibrational relaxation
were comparable to the induction times. The results indicated that in normal studies
irogen–oxygen ignition kinetics no effect of slow vibrational relaxation will be observed.

Introduction

tudies of the hydrogen–oxygen reac-
temperatures have been reported in
. For the case of pressures low enough
ecular reactions can be disregarded,
bsence of wall effects, they have con-
the dominant reactions of the induc-
are:

$$H_2 + O_2 = 2 OH \ (or \ H, O) \qquad (0)$$

$$H + O_2 = O + OH \qquad (1)$$

$$O + H_2 = H + OH \qquad (2)$$

$$OH + H_2 = H + H_2O. \qquad (3)$$

all result of this branching-chain
exponential growth of chain-carrier
ons with little release of heat. Sub-
ower termolecular reactions lead to
ical equilibrium and the release of
issions of this set of reactions, with
o additional experimental work, have
shed.[1-6]

Theoretical Treatment

to investigate the agreement between
tion of the induction period in terms
—
erformed at The University of Texas.

of Reactions (0)–(3) and experimental results, a
solution of the rate equations for these reactions
is required under conditions appropriate to the
experimental range of temperature, pressure,
and composition. In an early paper using tech-
niques similar to those employed here, Schott
and Kinsey[1] employed partial steady-state ap-
proximations[8] and assumed constant hydrogen
and oxygen concentrations in order to derive an
expression for the rate of growth of hydroxyl-
radical concentration. This led to a relation be-
tween oxygen concentration, induction time, and
temperature, which could be compared with their
experimental results. A different approach taken
was numerical integration of the rate equations
under the constraint of constant shock flow.[6,1]

The partial steady-state approximation used
by Schott and Kinsey, and also in previous treat-
ments of the induction period reactions for other
kinds of experiments,[4] was based on the following
considerations: Since Reaction (1) is 17 kcal
endothermic, whereas Reactions (2) and (3) are
about thermoneutral or exothermic ($\Delta E_2 = 3$ kcal,
$\Delta E_3 = -16$ kcal), it w assumed that Reaction
(1) was rate controlling and that the partial
steady-state approximation could be applied to
the concentrations of O and OH. Recent experi-
mental work,[3,7] however, has shown that the
rate coefficients of Reactions (1) and (2) are

actually about equal in the temperature range of interest here, and that the partial steady-state approximation cannot be applied to the concentration of O. This means that the analysis used by Schott and Kinsey is applicable only when the ratio of hydrogen to oxygen is very large.

We solved the system of rate equations for Reactions (0)-(3) without steady-state approximations or assumptions about the values of the rate coefficients. The rate equations are

$$d[OH]/dt = [H][O_2]k_1 + [O][H_2]k_2$$
$$- [OH][H_2]k_3 + 2[H_2][O_2]k_0, \quad (4)$$

$$d[O]/dt = [H][O_2]k_1 - [O][H_2]k_2, \quad (5)$$

$$d[H]/dt = [O][H_2]k_2 + [OH][H_2]k_3$$
$$- [H][O_2]k_1. \quad (6)$$

During all but the very last part of the induction period, when Reactions (0)-(3) no longer suffice to describe the reaction system, the concentrations of hydrogen and oxygen remain constant. Equations (4)-(6) then can be written

$$dx/dt = za + yb - xc + 2R_0, \quad (7)$$
$$dy/dt = za - by, \quad (8)$$
$$dz/dt = yb + xc - za, \quad (9)$$

where $x = [OH]$, $y = [O]$, $z = [H]$, and a, b, c and R_0 are constants at a given temperature and starting composition. The initial conditions are $x = y = z = 0$. The solution is

$$x = \text{coef } A \exp (B_A \cdot t) + \text{coef } B \exp (B_B \cdot t)$$
$$+ \text{coef } C \exp (B_C \cdot t),$$

where

$$B_A = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}\phi$$

$$B_B = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}(\phi + 2\pi)$$

$$B_C = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}(\phi + 4\pi)$$

$$\phi = \cos^{-1} \frac{2(a+b+c)^3 - 9(a+b+c)bc - 54\,abc}{2\{-[3bc - (a+b+c)^2]^2\}^{1/2}}.$$

$$
\begin{bmatrix} \text{coef } A \\ \text{coef } B \\ \text{coef } C \end{bmatrix}
=
\begin{bmatrix}
1 & 1 & 1 \\
\dfrac{B_A + c}{2b + B_A} & \dfrac{B_B + c}{2b + B_B} & \dfrac{B_C + c}{2b + B_C} \\
\dfrac{(B_A + b)(B_A + c)}{a(2b + B_A)} & \dfrac{(B_B + b)(B_B + c)}{a(2b + B_B)} & \dfrac{(B_C + b)(B_C + c)}{a(2b + B_C)}
\end{bmatrix}^{-1}
\begin{bmatrix} 0 \\ R_0/b \\ R_0/a \end{bmatrix}
$$

The constants appearing in the solution can be computed readily for any given temperatures, compositions, and rate coefficients.[14]

This solution incorporates assumptions of constant temperature and reactant concentration, ignores the fact that the experiments are actually performed in flowing gas, and allows chain initiation only by formation of OH. The last assumption is, in fact, not necessary; the solution is only slightly complicated by allowing H and O to be produced in initiation steps. There appears to be no gain in doing this at present, however, since little is known about the homogeneous reactions producing chain centers, and the interpretation of our results would be unaffected thereby. There is, likewise, little prospect that eliminating the other assumptions by analytical means, if it is possible at all, would be of advantage for present purposes. This can be shown by comparing the rate of increase of OH concentration in a shock-tube experiment, as computed using the analytic solution with a straightforward numerical integration of the rate equations with-

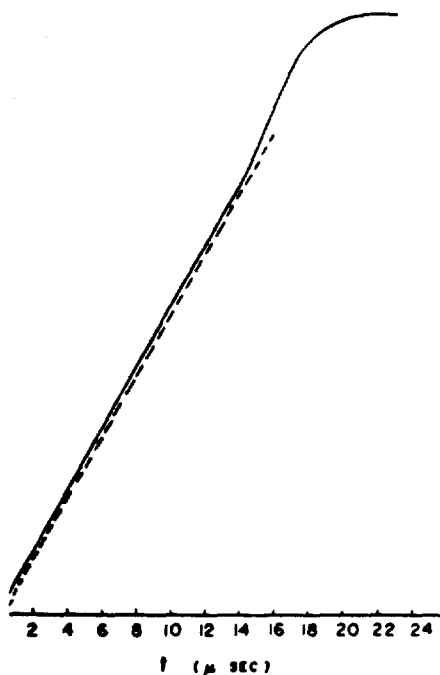out simplifications given by Schott and Kinsey. Figure 1 shows that the two solutions give identical results until well after the observed end of the induction period.

Similar treatments of the induction period kinetics have been presented by other authors.[4,5,9] They have shown that there are several kinds of simplifications which can be made in the equations. Two of the three roots are negative, and can be shown by direct calculation to give no contribution, even as transients, to the physically significant growth of radical concentrations. One has only to consider, therefore, the single positive root. The constants appearing in the equations can then be examined for size under a given set of experimental conditions, and superfluous ones omitted from the computation. One can then search for algebraic simplifications, and obtain expressions which can be plotted for comparison with experimental data, and inspected for insight into the chemical kinetics.

We have chosen an alternative procedure. For presentation of experimental data, a graph of

• t_i versus inverse temperature was
y Schott and Kinsey to be useful. It will
ater that such a plot has little theoretical
nce, but it serves well for inspection of
nt between predictions and experiments,
l allow the present experiments to be
d with the results of Schott and Kinsey.
re, our computational procedure was
l to develop theoretical relationships
$\log [O_2] \cdot t$, and $1/T$ for various experi-
mixtures and various sets of trial rate-
at expressions. The complete solution
grammed for a digital computer, and
f t_i were computed as the time between
ating and attainment of OH concentra-
ar 10^{-4} moles per liter, which is assumed
e detection threshold of our apparatus.[18]
an then determine the dependence of the
n-period reactions on concentration of
n and oxygen in the following way. The
ag rate can be written formally as

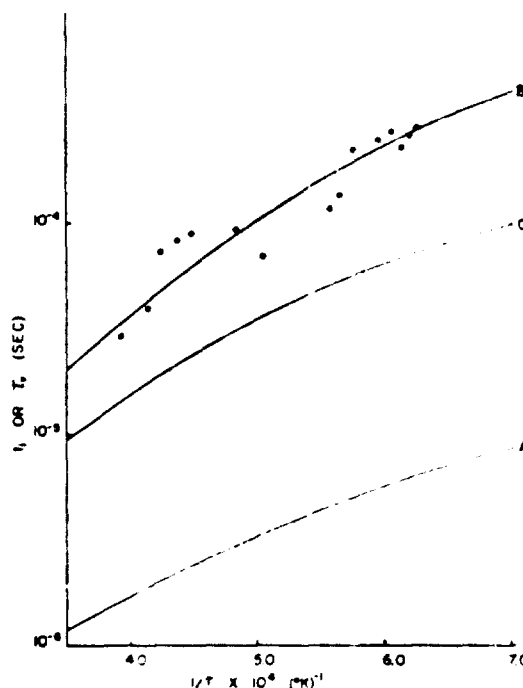$$d(\log x)/dt = k[O_2]^m[H_2]^n.$$

FIG. 2. Comparison of experimental induction
times with calculated vibrational relaxation times
for oxygen. Solid circles are measured induction
times for Ar:H₂:O₂ = 98:1:1. Curve A, vibrational
relaxation time for He:Kr:D₂:O₂ = 68:30:1:1.
Curve B, vibrational relaxation time for Kr:D₂:O₂ =
98:1:1. Curve C, vibrational relaxation time for
Ar:D₂:O₂ = 98:1:1. Starting pressure in each case,
10 Torr.

Integrated from shock heating to the observed
end of the induction period, assumed to be a
certain chain-center concentration, this yields

$$k[O_2]^m[H_2]^n \cdot t_i = \text{constant}.$$

or, in logarithmic form,

$$\log (\text{constant}) = \log k + m \log [O_2]$$
$$+ n \log [H_2] + \log t_i.$$

For one concentration held constant, the slope
of $\log 1/t_i$ versus $\log [\ ]$ for the other concentra-
tion gives m or n. In this way, the effective
molecularity of the induction-period reactions
can be determined from the experimental values
for the rate constants for Reactions (1), (3).

1. Comparison of analytic solution with
al integration of rate equations. Rate coeffi-
nd experimental conditions identical with
Fig. 2, Ref. 1. - - -, analytical solution;
merical integration.

Vibrational Relaxation Effects

At the upper end of the temperature range
studied in our experiments, the induction periods
begin to be so short that they approach the

vibrational relaxation time of oxygen. The question then arises as to whether the rates of Reactions (0) or (1) may be affected by the finite rate of equilibration of the first and second vibrational levels of oxygen, which are populated, at 2000°K, with 22% and 7%, respectively, of the total oxygen. Recently, accurate experimental data have become available on the efficiency of various collision partners for vibrational equilibration of oxygen.[10] A study was made to determine if there would be a possibility of observing the induction periods of the hydrogen–oxygen reaction at various degrees of vibrational equilibration of oxygen.

For the usual composition range employed in this and other shock-tube studies of the hydrogen–oxygen reaction, the greatest contribution to the oxygen relaxation comes from collisions with hydrogen, even when hydrogen is present in concentrations lower than 1%. This concentration is about the lower limit for accurate measurements of induction times in our apparatus. Calculation showed that it would not be possible to obtain any conditions where the induction time would be both shorter than the vibration relaxation time and still measurable with 1% hydrogen in the experimental mixture. A different situation is obtained when deuterium is substituted for hydrogen. The large increase in reduced mass for deuterium oxygen collisions slows down the calculated vibrational relaxation times to the point where they do indeed become as long as induction times, under conditions accessible to study in our apparatus. Additional lengthening

of the relaxation times is obtained by using krypton rather than argon as the diluent gas. In Fig. 2, the calculated vibrational relaxation times for two deuterium oxygen mixtures, one diluted with krypton and one diluted with krypton and helium, are compared with induction times for 10 Torr starting pressure. It was necessary to add krypton to the helium in order to obtain sufficiently high temperatures with our apparatus. The induction times in Fig. 8 are our results for an experimental mixture containing 1% hydrogen, 1% oxygen, and 98% argon. Relaxation times for krypton were obtained by extrapolation of experimental data for helium and argon. Relaxation times for deuterium were assumed to be the same as for helium, according to the suggestion by White.[13]

Experimental

The data presented here are induction periods in hydrogen–oxygen argon mixtures heated to reaction temperatures in the range 1400°–2400°K by incident shock waves. Starting pressures ranged from 5 to 15 Torr, with most of the experiments at 10 Torr. The induction period was experimentally defined as the time between shock heating and first observable trace of hydroxyl-radical concentration, multiplied by the density ratio in the shock to convert from observer to gas time.

Our apparatus is of conventional design (Fig. 3). The shock tube was constructed of 1.75 in. × 4 in. aluminum tubing. A series of flush, de-
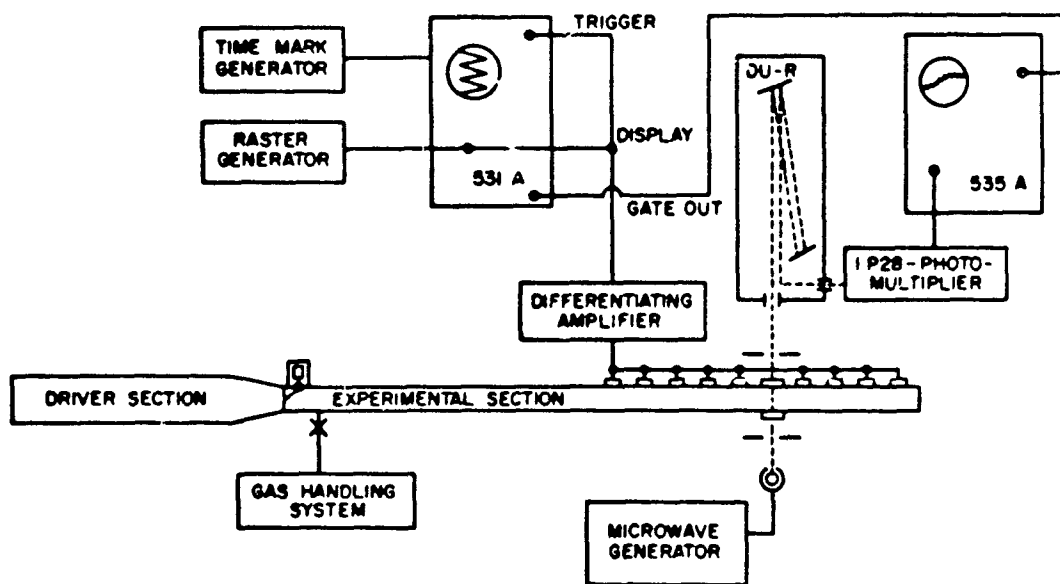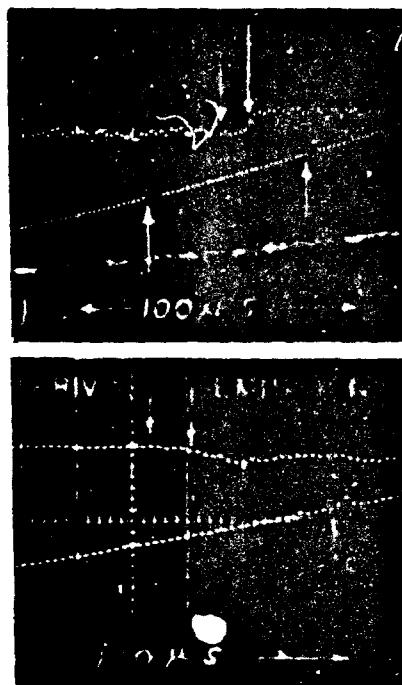

FIG. 3. Block diagram of apparatus.

Upper photograph: Absorption of 3067 Å OH. The diagonal trace records signals ance gauges. Experimental conditions :O_2 = 98:1:1; starting pressure, 10 Torr; perature, 2350°K. Lower photograph: om OD, triangular 30Å bandpass cen- 080 Å. Experimental conditions were = 98:1:1; starting pressure, 10 Torr; erature, 2480°K.

tinum resistance gauges, spaced on of the observation station, provided velocity measurements. The amplified e displayed together with time marks sweep oscilloscope. Shock velocities
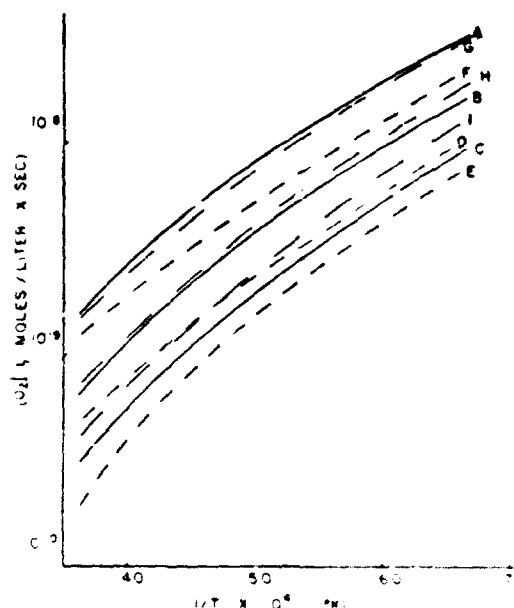

FIG. 5. Sensitivity of computed lines to variation of input-rate coefficients and cutoff concentration. Data for each line from Table II.

were computed by graphical analysis of the raster sweep photographs. Arrival of the shock wave at the observation point could be measured to about ±1 microsecond. The observation station was a pair of flush quartz windows on opposite sides of the shock tube.

The lamp for absorption measurements consisted of a microwave discharge (2.45 gc, 100 W) in about 10 Torr argon containing a trace of bismuth vapor.[11] The bismuth resonance line at 3067 Å, which coincides with the R_210 line of the 0-0 transition of the $^2\Sigma$–$^2\Pi$ system of OH, was isolated after collimation by slits with a Beckman DU monochromator, and the intensity measured

TABLE I

Composition of experimental mixtures

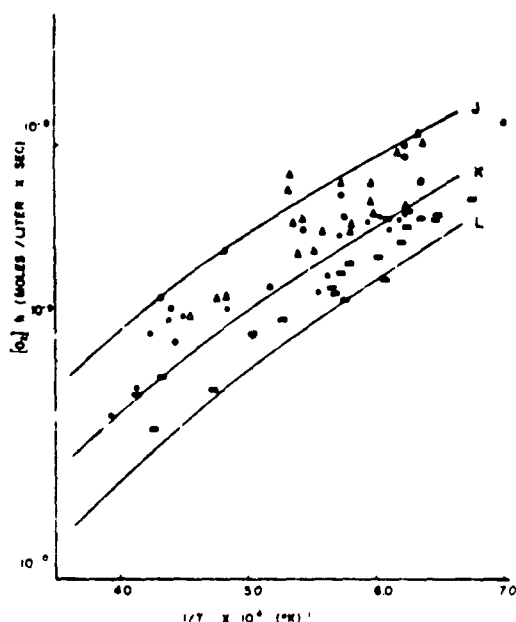| Hydrogen	Oxygen	Deuterium	Argon	Krypton	Helium	Ratio
0.032	0.010	0	0.958	0	0	3.2
0.020	0.010	0	0.970	0	0	2.0
0.010	0.010	0	0.980	0	0	1.0
0.0029	0.010	0	0.987	0	0	0.29
0.0017	0.010	0	0.988	0	0	0.17
0	0.010	0.010	0	0.98	0	1.0
0	0.010	0.010	0	0.30	0.68	1.0
0.010	0.030	0	0.960	0	0	0.33

Fig. 6. Induction times for OH absorption. Solid triangles, $H_2:O_2 = 0.17:1$; open triangles, $H_2:O_2 = 0.29:1$; open circles, $H_2:O_2 = 1:1$; open rectangles, $H_2:O_2 = 2:1$; solid rectangles, $H_2:O_2 = 3:1$; solid circles, $H_2:O_2 = 1:3$.

with a 1P28 photomultiplier. The anode signal was applied to the grid of a cathode follower, the output was adjusted for about 2 μsec response time, and displayed as a single sweep on a Tektronix 535A oscilloscope. For measurement of short induction periods, the output of the photomultiplier was displayed on an oscilloscope with a trace chopped at a crystal-controlled
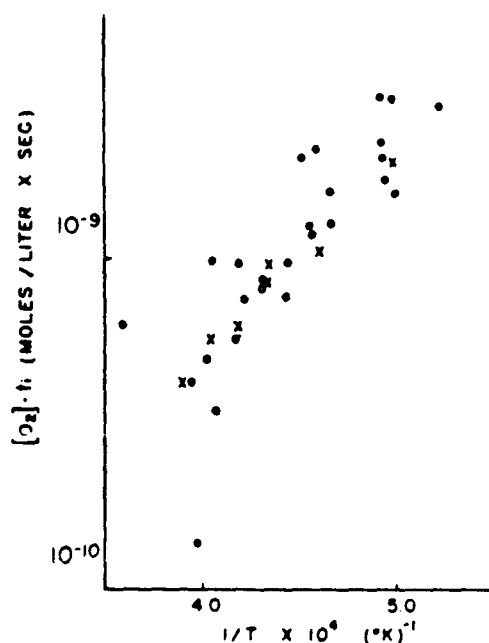

Fig. 7. Induction periods to onset of $2\Sigma-^2\Pi$ (0–0) emission in vibrational relaxation experiments. Crosses, $Ar:H_2:O_2 = 98:1:1$; open circles, $He:Kr:H_2:O_2 = 68:30:1:1$; solid circles, $Kr:D_2:O_2 = 98:1:1$.

frequency of 1 mc, to allow simultaneous recording of velocity markers and absorption or emission on one photograph. A sample oscillogram is shown in Fig. 4.

Gas mixtures were prepared manometrically in a conventional vacuum system. Commercial cylinder gases were used without purification.

TABLE II

Input data for computations

| Line	$[H_2]/[O_2]$	Cutoff	$\log A_0$	E_0	$\log A_1$	E_1	$\log A_2$	E_2	$\log A_3$	E_3
A	0.33	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
B	1.0	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
C	3.0	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
D	1.0	10^{-8}	11.0	70,000	11.86	16,900	9.9	7700	10.8	5900
E	1.0	10^{-8}	11.0	60,000	11.86	16,900	9.9	7700	10.8	5900
F	1.0	10^{-8}	10.0	70,000	11.36	16,900	9.9	7700	10.8	5900
G	0.33	10^{-8}	11.0	70,000	11.36	16,900	9.9	7700	10.8	5900
H	1.0	10^{-8}	11.0	70,000	11.36	16,900	9.9	7700	10.8	5900
I	3.0	10^{-8}	11.0	70,000	11.36	16,900	9.0	7700	10.8	5900
J	0.33	0.3×10^{8}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900
K	1.0	0.3×10^{-8}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900
L	3.0	0.3×10^{-8}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900

lists the compositions of the mixture

Results

nsitivity of theoretical lines for the $[O_2] \cdot t$, vs inverse temperature to a input rate constants and OH appearxntration, is shown in Fig. 5. Starting · input rate constants were taken from y article of Kaufman and Del Greco[3] suggestions of Baldwin[12] and Clyne.[7] rerimentally measured induction periods hydrogen–oxygen mixtures are shown The calculated lines correspond to the the rate constants given in Table II. on periods in deuterium–oxygen mixe measured to onset of OD emission at a Fig. 7, the results for the two different ital mixtures are shown, together with rents of the induction period determined nission at 3070 Å for a $H_2 + O_2 + 98$ re. .tion of the quantities m and n is illus- Fig. 8.

Discussion

sults presented in Fig. 6 demonstrate iction times in the hydrogen–oxygen n shock waves depend on the concen-
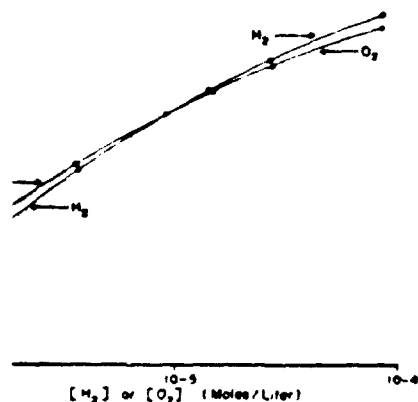
Investigation of effective molecularity of period reactions. Slope of H_2 curve yields ty for H_2, slope of O_2 curve yields molec- O_2. Temperature, 1800°K. Starting pres- orr for 98:1:1 mixture, and adjusted to reactant concentration constant for other

trations of both hydrogen and oxygen. They indicate also that the degree of dependence on composition and temperature can be predicted in reasonable agreement with experiment using rate-coefficient expressions for the elementary reactions involved that are in accord with previous experimental studies.

It is significant that, for reasonable values of appearance concentration and rate coefficients, the assumed induction period scheme allows the calculation of induction periods which reproduce both the temperature and concentration dependence of the reaction. Upon examination of the sensitivity of the solution to variation of the rate-coefficient parameters and appearance concentration, it is found that the slope, position, curvature, and composition dependence of the plotted $\log[O_2] \cdot t$, values depend strongly on the set of rate-coefficient parameters, except that k_3, being substantially greater than k_2 under all conditions, has little effect on the predicted curves. Too high a value for k_0 has the end effect of curving the plotted induction periods more strongly downward at high temperatures, since this causes the linear portion of the OH-concentration increase to continue to higher OH concentrations. The activation energy given to k_1 affects the slope of the calculated lines, while that given to k_2 affects only the position of the lines. This is a consequence of the fact that the activation energy of k_1 is considerably larger than the activation energy of k_2. It would be possible to reproduce the data of our experiments with other than the rate coefficient parameters indicated in Table II; one then loses, however, the correct extrapolations to data obtained in experiments at lower temperatures.

In the experiments performed to test for vibrational relaxation effects, a clear lengthening of the induction period for the vibrationally cold mixture can be seen. The scatter in the results for the vibrationally cold mixture appears to be greater than for other mixtures. This may be an effect of driver-gas mixing due to nonideal diaphragm rupture, as has been noted in other sensitive shock-tube experiments. It is clear from the magnitude of the induction period lengthening that no effect of vibrational relaxation will be observed in mixtures containing hydrogen and argon.

The effective molecularity of the induction period reactions depends on the composition of the reacting mixture and the temperature. Values of m and n under typical conditions of temperature (1800°) and composition are found to be $0.4 < m < 0.6$, $0.5 < n < 0.8$. The dependence upon oxygen concentration, for the temperature range of these experiments, is less than the dependence upon hydrogen concentra-

tion for equivalence ratios within a factor of 5 from stoichiometric. At lower temperatures, the reverse situation prevails, due to the higher activation energy of k_1. For the general case, it may be concluded that the rate of the branching-chain reactions depends on the concentrations of both hydrogen and oxygen, and that the degree of dependence is a function of temperature and of composition over all conditions normally encountered in the study of this reaction in the high-temperature, low-pressure region.

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14. Note added in proof: This form of the solution is for three real roots. Imaginary roots also occur for physically realizable conditions.
15. Note added in proof: We have subsequently determined that the correct threshold for our apparatus is 3×10^{-7} moles/liter. This finding necessitates some revision of the rate coefficient expressions, which will be reported at a later date.

COMMENTS

Dr. M. A. Khan (Shell Research Ltd., Thornton): I would like to ask about the activation energy of the initiation reaction

$$H_2 + O_2 \xrightarrow{E_i} OH + OH.$$
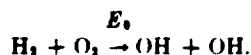
In his well known book *Chemical Kinetics and Chain Reactions*, Semenov quotes $E_i = 62$ kcal mole^{-1}, a value derived from the Haber mechanism, using Hinshelwoods' data. Again, in 1945, Semenov derived a value of 45 kcal mole^{-1} from Kowalsky's data. We now know that the Haber mechanism is obsolete. Could Gardiner give any reasons for not using the figure of 45 kcal mole^{-1}, and is there really any theoretical or experimental basis for the figure of 70 kcal mole^{-1}, which he uses in his paper?

Prof. W. C. Gardiner, Jr. Very little information about the rate coefficient for homogeneous chain initiation is available, and the assignment $H_2 + O_2 = 2 OH$, with the rate parameters given in our paper should be regarded only as a reasonable guess. At high temperatures, thermal dissociation of hydrogen, for which reliable rate coefficients are now available [Sutton, E. A.: J. Chem. Phys. 36, 2923

(1962)], appears to be faster than any other initiation process. Semenov suggests (*Some Problems in Chemical Kinetics and Reactivity.* Vol. 2, p. 151, Princeton University Press, 1959) that the early data of Kowalsky, if interpreted in terms of homogeneous chain initiation, yield an order-of-magnitude rate constant of 10^{-22} for $H_2 + O_2 = 2 OH$, or $H_2 + O_2 = HO_2 + H$, at 800°K. Belles has interpreted the data of White and Moore (this Symposium, p. 785) for rich mixtures, and finds that 45 kcal appears to be a reasonable activation energy for the initiation step. Hirsch and Ryason [J. Chem. Phys. 40, 2051 (1964)] find that experimental values for ignition delay can be reproduced computationally with chain initiation via thermal dissociation of hydrogen only, which has an activation energy of 103 kcal. Careful ignition-delay measurements in rich mixtures over a wide temperature range, analyzed with a procedure similar to that used by Dr. Belles, might provide more information on this subject. Lacking more and better data, however, there are no firm grounds for identifying homogeneous initiation with a specific elementary reaction or for assigning an activation energy.